Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 771

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January 1999

Submitted to
Annual Meeting
Pulp and Paper Technical Association of Canada
(formerly CPPA)
Montreal, Quebec, Canada
January 26-29, 1999

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A COMPARATIVE EVALUATION OF LOW-AOX HARDWOOD KRAFT PULP BLEACHING SEQUENCES

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ABSTRACT

Southern U.S. hardwood kraft pulp was bleached by several low-AOX sequences. At a given charge of ClO_2 in the initial brightening (D_1) stage, pulp that had been oxygen delignified prior to ClO_2 delignification was significantly brighter than pulp that had not been oxygen delignified. Bleachability in the D_1 stage was not significantly affected by normal levels of filtrate carryover into or beyond the D_0 stage or by substitution of Cl_2 or O_3 for part of the ClO_2. In terms of the total ClO_2 requirement to reach 89-90 brightness, sequences may be ranked as follows: OD(EPO)DP < O(Z/D)(EPO)DP < (D/C)(EPO)DED = (D/Z)(EPO)DED = OD(EPO)DD < D(EPO)DED < OD(EPO)D. In an additional stage following an OD(EPO)D sequence, H_2O_2 and ClO_2 were equally effective on a weight basis but ozone was less effective. Combined effluent AOX values were close to those predicted by an empirical model, which, in effect, predicts that 11-13% of the Cl atoms added in the first bleaching stage and 2% of the Cl atoms added in subsequent stages will emerge as AOX.

INTRODUCTION

Many kraft mill bleach plants are about to be reconfigured, in response to increasingly stringent effluent regulations, as exemplified by the U.S. Environmental Protection Agency's "Cluster Rule." A major consideration in selecting the bleaching sequences to be implemented is the amount of adsorbable organic halide (AOX) generated. Consequently, there is considerable interest in comparatively evaluating sequences that may be expected to release low levels of AOX, with due regard to chemical consumption and pulp quality.

This paper describes the results of such an evaluation of elemental chlorine free (ECF) sequences which, although based primarily on the use of chlorine dioxide, also employ hydrogen peroxide and, in some cases, ozone. The starting materials for the study were unbleached hardwood pulp samples obtained from the a single fiberline in a southern U.S. kraft mill. Samples taken both before and after the mill's medium consistency oxygen delignification stage were used, allowing us to effectively evaluate sequences with and without oxygen delignification.

An objective of the study was to maximize the applicability of the results by simulating real systems as closely as possible. Since all such systems employ interstage washers that are less than perfect, we simulated washer inefficiency by adding to each stage a measured amount of "carryover," filtrate from the preceding stage, or in the case of the first stage, black liquor or oxygen stage filtrate. In the case of the D(EPO)DED sequence, control experiments were also run to evaluate the effect of carryover. The amounts of carryover used were chosen to represent typical commercial washer efficiencies.

The sequences studied were (D/C)(EPO)DED, D(EPO)DED, (D/Z)(EPO)DED, OD(EPO)D, OD(EPO)DD, OD(EPO)DP, OD(EPO)DZ, and O(Z/D)(EPO)DP. All were evaluated with realistic levels of filtrate carryover into each stage. We also evaluated the D(EPO)DED sequence without filtrate carryover from any bleaching stage to the next and denoted that by DW(EPO)DED. Note that the single "W" in this designation indicates that there was "perfect" washing after every stage, not just the first. Another case studied was that in which both liquor carryover into the first stage and filtrate carryover from one bleaching stage to the next were eliminated, designated WDW(EPO)DED. Information was also obtained on shorter sequences corresponding to the first three or four stages of some of these sequences. All bleaching was done with a first-stage kappa factor of 0.20, based on the kappa number of the thoroughly washed unbleached pulp, and all (EPO) stages were done with the same conditions and chemical charges.

EXPERIMENTAL

The unbleached hardwood kraft pulp was first centrifuged to obtain full strength filtrate for use as carryover. After thorough washing, the pulp had a kappa number of 13.0. Before bleaching, an amount of filtrate equivalent to 10 kg dissolved solids per ton of pulp was added back to the pulp. The kappa number of the pulp after filtrate addition was 14.0. Pulp taken downstream of the mill's oxygen stage was treated similarly. Its kappa number after thorough washing was 9.3, and after re-addition of filtrate equivalent to 10 kg solids per ton, the kappa number was 10.5.

The (DC) stage was done in a stirred batch reactor at 3.5% consistency and 50°C for 45 min, at 0.20 kappa factor based on the washed kappa number. The level of substitution of ClO_2 for Cl_2 was 70% and the ClO_2 was added 15 s before the Cl_2. Chlorine dioxide delignification (D_0) stages were run under the same conditions of time, temperature, and consistency as the (DC) stage. (D/Z) stages were run in a CRS high-shear laboratory reactor at 3.5% consistency and 50°C. After injection of ClO_2 solution, the pulp was mixed at 1500 rpm for 20 s, then again for 10 s at intervals of 5 min. Ozone was injected 15 min after ClO_2 injection and the pulp was mixed at 1500 rpm for 20 s initially and at 5-min intervals thereafter for 30 min. (Z/D) stages were run in similar fashion, the O_3 being added first, followed immediately by 20 s of mixing at 1500 rpm, and additional periods of mixing at intervals of 5 min. The ClO_2 was added 15 min after O_3 and mixed as in the (D/Z) stage.

The (EPO) stage was run at 10% consistency and 75°C for a total of 75 min in a horizontal-shaft peg mixer. Ten percent of the filtrate from the previous stage was added to the pulp, which was then preheated to 75°C in a microwave oven. Hydrogen peroxide was added to the preheated pulp in the mixer, which was then pressurized with oxygen to a gauge pressure of 35 psi, following which the pressure was decreased to 0 over a period of 15 min. The pulp was held in the reactor for an additional 60 min.

Chlorine dioxide brightening (D_1 and D_2) stages were conducted at 10% consistency in polyester bags, normally after adding 20% of the filtrate from the preceding stage. The pH of the pulp was adjusted to the desired initial value and the ClO_2 was added. The bag was then sealed, heated in a microwave oven and transferred to a water bath maintained at the reaction temperature for 3 h.

Caustic extraction (E_2) stages after ClO_2 brightening stages were conducted at 10% consistency and 75°C for 1 h, normally in the presence of 20% of the filtrate from the preceding stage.

Final P stages were done in a teflon-coated Quantum mixer at 10% consistency in the presence of 20% of the filtrate from the previous stage. The total reaction time was 105 min. Nominally, the temperature was maintained at 110°C for 15 min, following which the reactor was cooled to 90°C by venting and the reaction continued for another 90 min. All stages were run in the presence of 0.1% $MgSO_4$ and 0.1% DTPA.

Final ozone stages were run in the CRS reactor at 32% consistency and room temperature for 15 min. Upon ozone injection, the reactor was mixed at 500 rpm for 20 s and then again at 5 min intervals. The total reaction time was 15 min.

The individual stage filtrates were collected and refrigerated until the sequence was complete. A sample of combined filtrate was prepared using individual filtrates in the proportions in which they were released, calculated from stage consistencies and carryover levels. Filtrate samples for AOX analysis were treated with $Na_2S_2O_3$, pH-adjusted to < 2 with concentrated HNO_3 and stored at 4°C. Filtrate samples for COD were pH-adjusted to < 2 with 4N H_2SO_4 and stored at 4°C. Immediately after combining and pH adjustment, the samples were refrigerated and shipped in insulated containers. Testing was usually completed within 48 hours.

All filtrate tests were done by Savannah Laboratories, Mobile, AL, according to the following methods: AOX-EPA Method 1650 rev. B[1] and COD-Standard method 5220C.[2]

RESULTS

In what follows, the results are described first with reference to comparisons of the effectiveness of the various types of stages used in the first position in the bleaching sequence (excluding oxygen), then with reference to the first brightening stage, and finally the various full sequences are compared in terms of chemical consumption, pulp quality indicators, and effluent characteristics.

Delignification Partial Sequence

Figure 1 and Table I show the results of delignifying either brownstock or oxygen delignified pulp by various partial sequences of the type S(EPO), in which "S" represents (D/C), D, (D/Z), OD or O(Z/D). In the partial sequence designations shown, the symbol "W" indicates that the pulp is thoroughly washed to eliminate any carryover into the following stage. All bleaching was done with a first-stage kappa factor of 0.20, based on the kappa number of the thoroughly washed unbleached pulp. Inclusion of black liquor or oxygen stage filtrate effectively increased the kappa number of the unbleached pulp, effectively reducing the kappa factor to about 0.18, as shown in the table. Since this value is somewhat lower than values often used in commercial ECF bleaching of hardwood pulps, the extracted kappa numbers shown in Figure 1 and Table I are correspondingly higher.

After (DC)(EPO), the kappa number was 3.8 when the terminal pH was 3.3 in the (DC) stage, and fell to 3.1 when the (DC) pH was decreased to 2.5. Substituting ClO_2 for all of the Cl_2 reduced the extent of delignification, increasing the extracted kappa number from 3.1 to 6.0. Eliminating carryover of filtrate from the D stage to the (EPO) stage had no effect on delignification. Eliminating both black liquor carryover to the D stage and carryover to the (EPO) stage improved delignification, causing the extracted kappa number to drop from 6.1 to 5.4. This decrease is attributable to the associated increase in effective kappa factor. Replacing 50% of the ClO_2 with ozone on an oxidizing equivalent basis (1 kg O_3/1.69 kg ClO_2) produced no change in the degree of delignification achieved, but required slightly more caustic in the (EPO) stage. The effectiveness of ozone could probably be improved by increasing the consistency, especially in the presence of carryover.

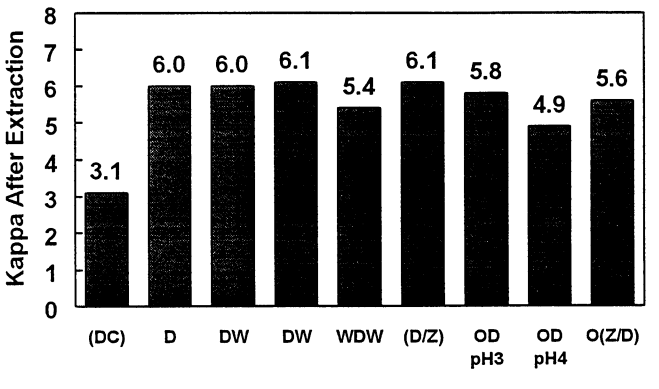

Figure 1. Kappa number after S(EPO) and OS(EPO) partial sequences in which S is an oxidative stage of the type indicated. Realistic levels of stage-to-stage carryover were used except where indicated by a "W," which indicates a perfect washing stage

Chlorine dioxide delignification of the oxygen delignified pulp gave a lower extracted kappa number than in the case of the brownstock, especially when the pH of the D stage was raised. Under these conditions, (which also resulted in a higher

TABLE 1
COMPARISON OF DELIGNIFICATION PARTIAL SEQUENCES INCORPORATING AN (EPO) STAGE

		First Stage						(EPO) Stage			
Unbleached Pulp Type	First Stage Type	ClO_2, % o.d. pulp	Cl_2, % o.d. pulp	O_3, % o.d. pulp	Spent Liq. Solids, % o.d. pulp	Effective Kappa Factor	Exit pH	NaOH, % o.d. pulp	Carryover, % of First Stage Filtrate	Exit pH	Kappa Number
Brownstock	(DC)	0.692	0.780	0	1	0.186	3.3	1.43	10	11.8	3.8
		0.692	0.780	0	1	0.186	2.5	1.30	10	11.5	3.1
	D	0.988	0	0	1	0.186	2.5	1.10	10	11.1	6.0
	DW	0.988	0	0	1	0.186	2.5	1.00	0	11.3	6.0
		0.988	0	0	1	0.186	2.6	1.00	0	11.3	6.1
	WDW	0.988	0	0	0	0.200	2.5	1.00	0	11.6	5.4
	(D/Z)	0.494	0	0.293	1	0.186	2.7	1.25	10	11.7	6.1
O_2 Delignified	D	0.707	0	0	1	0.177	2.5	1.00	10	11.6	5.5
		0.707	0	0	1	0.177	2.6	1.00	10	11.4	5.8
		0.707	0	0	1	0.177	3.9	1.00	10	11.9	4.9
	(Z/D)	0.354	0	0.210	1	0.177	2.8	1.20	10	11.8	5.6

Notes: 1. Kappa factor (washed pulp basis) 0.200 throughout.
2. 0.4% H_2O_2 in all (EPO) stages.

extraction stage exit pH) the extracted kappa number after OD(EPO) was 4.9, as compared to 6.1 after D(EPO). Relative to the initial kappa number, however, a slightly smaller percentage lignin removal is achieved in the case of the oxygen delignified pulp (47% as compared to 53% in the case of the brownstock). When the exit pH of the D stage was 2.5-2.6, slightly less delignification was achieved, the extracted kappa number being 5.5-5.8). Replacing 50% of the ClO_2 with ozone on an oxidizing equivalent basis (1 kg O_3/1.69 kg ClO_2) caused no change in the extent of delignification of the oxygen delignified pulp; the extracted kappa number remained at 5.6. There was, however, a slight increase in alkali consumption in the (EPO) stage. In these experiments, as in all others except the one mentioned above, the pH of the pulp was adjusted to 3.0 before the first stage of bleaching. It is not known whether increasing the pH of the (D/Z) and (Z/D) stages would have had a beneficial effect, analogous to that observed in the D stage on the oxygen delignified pulp.

Initial Brightening

In most cases, pulp emerging from an (EPO) stage was treated with 1% ClO_2. Exceptions included the (D/Z)(EPO)DED and OD(EPO)D sequences, for which several levels of ClO_2 application in the D_1 stage were evaluated, and sequences of the type OD(EPO)DS (S = D_2, P, or Z), in which only 0.4% ClO_2 was used in the D_1 stage.

It was hypothesized that, in all cases, the resulting brightness would be a function only of the ratio of the ClO_2 charge to the kappa number of the pulp after the (EPO) stage. To test this, we plotted the brightness after the D_1 stage against that ratio. The results are shown in Figure 2 for all sequences, including two versions of the D(EPO)DED sequence incorporating perfect washing after each bleaching stage. One, denoted DW(EPO)DED, was conducted with the addition of black liquor to the D_0 stage. Note that the single "W" in this designation indicates that there was "perfect" washing after every bleaching stage, not just the first. The other version, denoted WDW(EPO)DED, incorporated perfect washing before the D_0 stage as well as before every bleaching stage. As shown in Figure 2, the data can be divided into two groups, within each of which there was a strong correlation between the variables plotted. Samples that had been oxygen delignified prior to ClO_2 delignification were significantly brighter after applying a given charge of ClO_2 than those which had not been oxygen delignified. The latter all fell on a single line, from which it can be concluded that D_1 stage bleachability is not significantly affected by normal levels of filtrate carryover into or beyond the D_0 stage or by substitution of Cl_2 or O_3 for part of the ClO_2. Figure 2 also shows that there is a sharp reduction in the effectiveness of incremental additions of ClO_2 to the D_1 stage beyond a certain threshhold value of the ratio of charge to kappa number. This value is approximately 0.2 for brownstock and approximately 0.1 for oxygen delignified pulp.

Final Brightening with Chlorine Dioxide

Figure 3 shows the response to increases in the ClO_2 charge in the final stage for all sequences except those that ended with a P or a Z stage. In all cases where the sequence ended in DED, the results shown are for a D_1 stage ClO_2 charge of 1%. The (D/C)(EPO)DED sequence exhibited the highest brightness at a given final stage ClO_2 charge, followed very closely by the D(EPO)DED sequence. The latter sequence was not appreciably affected by the moderate levels of stage-to-stage carryover employed. It was similarly unaffected by inclusion of 10 kg/t of black liquor solids in the D_0 stage, in spite of the fact that black liquor solids caused a small but significant increase in the (EPO) kappa number.

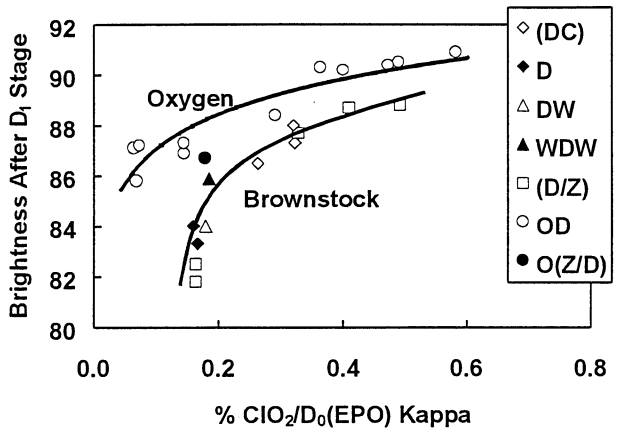

Figure 2. D_1 stage brightness response in partial sequences of the type S(EPO)D_1 and OS(EPO)D_1, in which S is a stage of the type indicated. The charge of ClO_2 is expressed as a ratio to the kappa number of the pulp entering the D_1 stage.

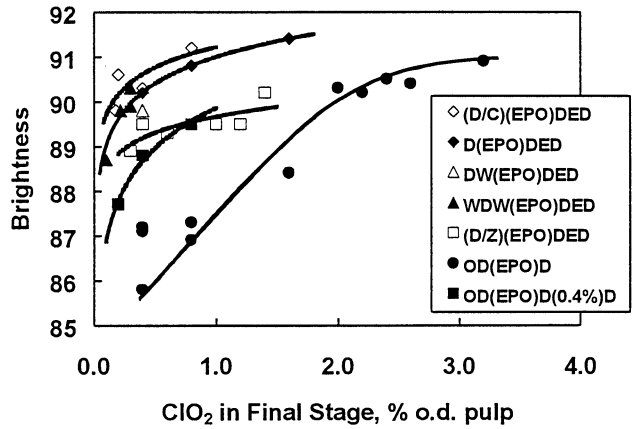

Figure 3. Response of final brightness to ClO_2 charge in final stage

Substitution of O_3 for half of the ClO_2 in the first stage appeared to decrease the brightness ceiling to approximately 90, as compared to an estimated value of about 92 when the oxidant in the first stage was 100% ClO_2. This apparent decrease in brightness ceiling may have resulted from the fact that the brightness of the D_1 pulp was 2.2 points lower than in the case of the D(EPO)DED sequence, since it has previously been shown that the D_2 stage brightness ceiling depends on D_1 stage brightness.[3] In spite of the difference in D_1 stage brightness, there was little or no effect of O_3 substitution on D_2 brightness at levels below 89. The brightness of (D/Z)(EPO)D pulp was easily raised from 82 to 89 with 0.3% ClO_2 in D_2. The observed replacement ratio of 1.7 is somewhat lower than the values reported earlier by Chirat and Lachenal.[4] It should be noted, however, that we made no attempt to optimize this sequence.

Pulps bleached by the OD(EPO)D sequence appear to be at a disadvantage when compared to the D(EPO)DED sequence on the basis of ClO_2 charge needed in the final stage to achieve a given brightness target, as in Figure 3. This is not a fair comparison, however, because the final stage pulp in the 5-stage sequence had already been substantially brightened by the application of 1% ClO_2 in a D_1 stage. The apparent disadvantage is smaller for the OD(EPO)DD sequence, but it still exists and is attributable to the fact that only 0.4% ClO_2 was used in the D_1 stage of OD(EPO)DD.

Fairer comparisons of sequences can be made on the basis of the total amount of ClO_2 applied in the brightening stages, as shown in Figure 4. Plotted in this way, the data divide themselves roughly into two groups, represented by the two curves shown. The upper curve is about 1 brightness unit above the lower one, a disparity that translates to a disparity in ClO_2 consumption of about 0.6% for a given brightness target. The upper curve represents the sequences D(EPO)DED (with or without filtrate carryover) and OD(EPO)DD, with the (D/C)(EPO)DED sequence tending to give brightnesses that are slightly above the curve. The lower curve represents the sequences OD(EPO)D and (D/Z)(EPO)DED. The O(Z/D)(EPO)D sequence gave a brightness slightly below the lower curve.

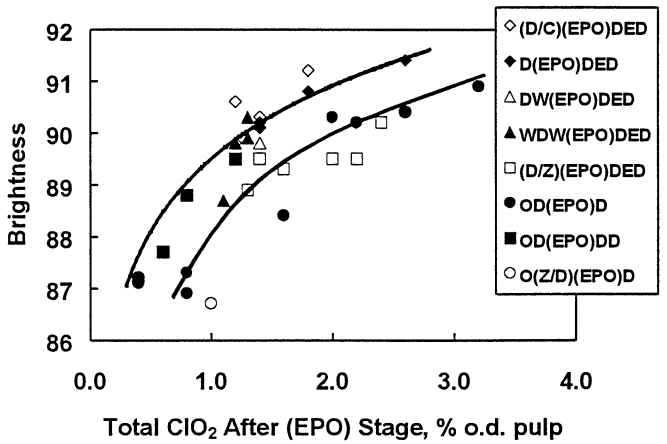

Figure 4. Brightness after full bleaching as a function of the total charge of ClO_2 in the brightening stages

In summary, the data presented above suggest several conclusions. Bleaching to high brightness in three stages can be achieved with much less final-stage ClO_2 after an oxygen stage than when no oxygen stage is present. The bleaching of oxygen delignified pulp can be accomplished in fewer stages than the bleaching of brownstock to similar brightness levels, although reducing the number of stages to three entails a slight increase of ClO_2 consumption in the brightening stages, which is partially compensated by a reduction in D_0-stage ClO_2 consumption. The results also suggest that partial substitution of O_3 for ClO_2 in the D(EPO)DED sequence has no effect on final brightness, except possibly at extremely high brightness levels. The brightness obtained by the D(EPO)DED sequence is relatively unaffected by normal levels of filtrate carryover from stage to stage.

Hydrogen Peroxide and Ozone as Final Brightening Stages

The usefulness of H_2O_2 or O_3 in the final stage of a four-stage sequence following oxygen delignification was evaluated by comparing each with ClO_2. Pulp delignified by an OD(EPO) partial sequence as described above was bleached with 0.4%

ClO_2 in a D_1 stage, giving a brightness of 85.8. This pulp was then further brightened in a final stage, without an intermediate alkali extraction, using a range of levels of application of ClO_2, H_2O_2, or O_3. In these experiments and the ones described below, H_2O_2 was applied in a short (15 min) high-temperature (110°C) stage, followed by a 90 min retention period at 90°C, as suggested by van Lierop *et al.*[5] The results, shown in Figure 5, demonstrate that H_2O_2 and ClO_2 were equally effective on a weight basis. Ozone, however, was less effective in brightening the pulp. This observation differs from that obtained in the bleaching of softwood pulp by Chirat *et al,*[6] who found ozone more than twice as effective as ClO_2 on a weight basis in this terminal position.

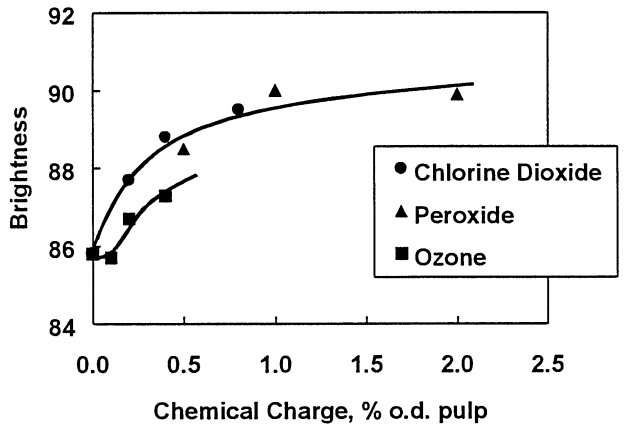

Figure 5. Brightening with ClO_2, H_2O_2, or O_3 in an additional stage after OD(EPO)D bleaching

Hydrogen peroxide was also evaluated as a final stage added to an O(Z/D)(EPO)D sequence. Pulp delignified by an O(Z/D)(EPO) partial sequence was bleached with 1.0% ClO_2 in a D_1 stage, giving a brightness of 86.7. This pulp was then brightened with several different charges of H_2O_2, giving the results shown in Figure 6.

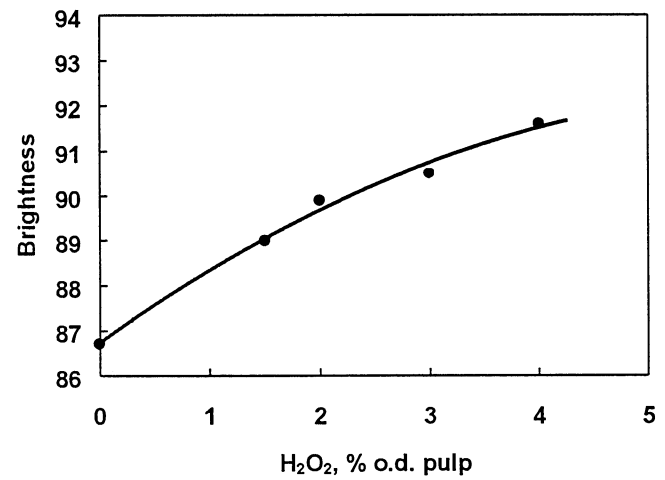

Figure 6. Brightening with H_2O_2 in an additional stage after O(Z/D)(EPO)D bleaching

A final brightness of 89 could be achieved with 0.6% H_2O_2 in the OD(EPO)DP sequence with 0.4% ClO_2 in the D_1 stage. The same final brightness in the O(Z/D)(EPO)DP sequence required 1.5% H_2O_2, even after using 1.0% ClO_2 in the D_1 stage. Interestingly, however, the data also suggest that O_3 substitution raises the brightness ceiling, making it possible to reach very high brightnesses with very large H_2O_2 charges.

Bleached Pulp Properties

Viscosity and brightness reversion of samples of fully bleached pulps from all sequences were measured, with the results shown in Table II. Brightness reversion (upon artificial aging for 1h in a forced air circulation oven at 105°C) was similar for all sequences, except that sequences ending with a H_2O_2 stage gave pulps with slightly improved brightness stability and the sequence ending with an O_3 stage gave poorer brightness stability. The latter observation differs fom that made by Chirat and Lachenal[4] when softwood pulps were treated with 0.2% O_3 after DEDED and OQZP sequences. These authors noted no deterioration in brightness stability, although they did observe that carbonyl groups were introduced in the final Z stage. It is possible that hardwoods respond differently than softwoods in this respect.

When ranked according to pulp viscosity, the sequences fell into two homogeneous groups. The low-viscosity group included the D(EPO)DED sequences with no carryover and sequences in which O_3 was used. The positive effect of carryover on final viscosity is surprising. The reason for the low viscosity when the pulps were well washed between stages is unknown, but could be related to buffering or radical trapping effects. The viscosities of the fully bleached oxygen delignified pulps were sensitive to the amount of ClO_2 applied in the D_1 stage. When this was 0.4%, as in the case of the OD(EPO)DD and OD(EPO)DP pulps, the viscosity was in the range 19–20 mPa.s, but when it was 1.8%, as in the case of the OD(EPO)D pulp, the viscosity was much lower, 11.1 mPa.s. Additional experiments with 0.8% and 2.0% ClO_2 in the D_1 stage gave viscosities of 17.9 and 10.3 mPa.s, respectively. In all of these experiments the terminal pH of the D_1 stage was controlled at or near a value of 4.0, which is generally considered to be the optimum value for brightening. Experiments in which the pH was allowed to fall to values in the range 2.3-2.8 gave viscosities 2-4 mPa.s higher than at pH 4, an observation that implicates hypochlorous acid as being responsible for the viscosity loss. Similar dependence of viscosity on ClO_2 concentration has been observed in the CEHHD bleaching of softwood kraft pulp by Teder and Tormund[7] and in the OD(EO)D bleaching of hardwood kraft pulp by Asplund and Germgard.[8]

Effluent Properties

Combined effluent samples were prepared for several of the sequences by mixing volumes of individual stage filtrates that were proportional to the volume released, based on consistency and corrected for carryover. The combined effluents were then analyzed for AOX and Chemical Oxygen Demand (COD). Predicted AOX values were calculated using an empirical model based on statistical analysis of AOX data from laboratory bleaching of softwood pulps.[9] The results of these analyses are shown in Table III. The AOX values were close to those predicted by the model, which, in effect,

predicts that 11-13% of the Cl atoms added in the first bleaching stage and 2% of the Cl atoms added in subsequent stages will appear in the bleach plant washer filtrates as AOX.

TABLE II

BLEACHED PULP PROPERTIES

Sequence	Bright-ness	Reversion	Viscosity, mPa.s
(DC)(EPO)DED	89.8	2.5	21.5
D(EPO)DED	90.1	2.3	20.4
DW(EPO)DED	89.8	2.2	15.1
(Duplicate bleach)	89.2	1.4	14.8
WDW(EPO)DED	90.3	3.4	14.2
(D/Z)(EPO)DED	89.5	2.8	14.9
OD(EPO)D	89.4	1.7	11.1
OD(EPO)DD	89.5	2.1	19.0
OD(EPO)DP	90.0	1.5	19.7
OD(EPO)DZ	86.7	7.4	15.7
O(Z/D)(EPO)DP	89.0	1.6	14.2

Note, however, that the amount of AOX in the final mill outfall (which the Cluster Rule limits to 0.623 kg/admt at bleached papergrade kraft mills) will be substantially lower than this value. This is due to partial (perhaps 30-45%) destruction by alkaline hydrolysis when the acid and alkaline filtrates are mixed, and further (perhaps 40-50%) destruction in the secondary biological treatment system. The results reported in Table III do not incorporate either of these effects because they are from measurements on untreated effluents that were combined under low-temperature conditions that prevent alkaline hydrolysis. COD values for the five-stage ECF sequences were higher than for the (D/C)-based sequence and elimination of black liquor carryover into the first stage decreased COD. The effluent from the O(Z/D)(EPO)DP sequence had the lowest AOX content as well as the highest COD value.

TABLE III

PROPERTIES OF COMBINED FILTRATES BEFORE TREATMENT

Sequence	Bright-ness	AOX, kg/admt	Predicted AOX, kg/admt	COD, kg/admt
(DC)(EPO)DED	89.8	1.45	1.31	30.9
D(EPO)DED	90.1	0.70	0.74	40.4
DW(EPO)DED	89.8	0.69	0.74	42.9
WDW(EPO)DED	90.3	0.74	0.73	34.3
(D/Z)(EPO)DED	89.5	0.60	0.54	43.4
OD(EPO)D	89.4	0.44	0.6	26.8
O(Z/D)(EPO)DP	89.0	0.24	0.32	60.8

Chemical Consumption

Although the individual sequences were not optimized with respect to chemical application levels in each stage, it may be assumed that the charges used were reasonably close to those that might result from a more rigorous optimization. It is therefore of interest to roughly compare the chemical consumption data for the various sequences. One such comparison is contained in Table IV, in which the basis of comparison is a total chemical cost calculation based on an assumed set of unit chemical costs. These were \$0.90/kg for ClO_2; \$0.75/kg forH_2O_2; \$1.10/kg for O_3; \$0.24/kg for NaOH; \$0.22/kg for Cl_2; and \$2.00/kg for DTPA. It should be noted that Table IV gives the chemical charges that were used in experiments that produced pulps with the actual brightness shown, and that these are not all the same. In all but one case, they range from 89.0 to 90.3, but any given sequence may be expected to show appreciable cost differences within this range. The cost figures must therefore be regarded as approximate and are intended only to provide a common basis for a rough comparison of the sequences. Subject to this caveat, and under the assumptions noted above, several observations may be made. All of the five-stage ECF sequences had virtually the same chemical costs, which were, surprisingly, unaffected by filtrate carryover at the levels investigated. The bleaching of oxygen delignified pulp could be accomplished in three stages at the same cost for chemicals (excluding any chemical cost associated with the oxygen stage itself). Addition of a final ClO_2 stage to the OD(EPO)D sequence allowed the oxygen delignified pulp to be bleached to a similar brightness at a chemical cost which was roughly 20% lower than for the three-stage sequence or the five-stage non-oxygen sequence. This saving would be even greater if an extraction stage were placed between the final two D stages. Addition of an H_2O_2 stage instead of a ClO_2 stage did not yield a similar saving, when the charge of H_2O_2 was 1% in the final D-stage. However, a reduction in the H_2O_2 charge to 0.5% caused only a minor loss in bleached brightness to 88.5, and a smaller loss in reverted brightness, while decreasing the bleaching chemical cost to a value comparable to that of the OD(EPO)DD sequence. Using an O_3 stage at this point did not appear to be feasible. Partial replacement of ClO_2 with O_3 increased chemical costs for the OD(EPO)DP sequence.

SUMMARY AND CONCLUSIONS

Southern U.S. hardwood kraft pulp was bleached by several low-AOX sequences. The results may be summarized in terms of degree of delignification achieved in the early part of the sequence, response to ClO_2 in the initial brightening stage, final brightening, bleached pulp properties, effluent properties and estimated chemical cost.

The kappa number after the first two stages of bleaching (excluding the oxygen delignification stage) was substantially lower when the first stage was a 70% substitution (DC) stage than when it was a D stage. It was unaffected by substitution of 50% of the ClO_2 in the first stage by the equivalent amount of O_3.

At a given charge of ClO_2 in the initial brightening stage, pulp that had been oxygen delignified prior to ClO_2 delignification was significantly brighter than pulp that had not been oxygen delignified. A corollary is that bleaching to high brightness in three stages can be achieved with much less final-stage ClO_2 after an oxygen stage than when no oxygen stage is present.

TABLE IV

SUMMARY OF CHEMICAL CONSUMPTION DATA

Unbleached Pulp Type	Sequence	No. of Stages	Chemical Charges, % o.d. pulp						Chem. Cost, $/odut	Actual Final Brightness
			ClO_2	Cl_2	H_2O_2	O_3	NaOH	DTPA		
Brownstock	(DC)(EPO)DED	5	1.892	0.78	0.4		1.93		26.38	89.8
	D(EPO)DED	5	2.388		0.4		1.40		27.85	90.2
	DW(EPO)DED	5	2.388		0.4		1.40		27.85	89.8
			2.388		0.4		1.40		27.85	89.2
	WDW(EPO)DED	5	2.388		0.4		1.40		27.85	90.3
	(D/Z)(EPO)DED	5	1.894		0.4	0.293	1.60		27.11	89.5
O_2 Delignified	OD(EPO)D	3	2.507		0.4		1.00		27.96	89.4
	OD(EPO)DD	4	1.907		0.4		1.05		22.68	89.5
	OD(EPO)DP	4	1.107		1.4		2.05	0.1	27.38	90.0
	OD(EPO)DZ	4	1.107		0.4	0.200	1.05		17.68	86.7
	O(Z/D)(EPO)DP	4	1.354		1.9	0.210	3.00	0.1	37.95	89.0

D_1 stage bleachability was not significantly affected by normal levels of filtrate carryover into or beyond the D_0 stage or by substitution of Cl_2 or O_3 for part of the ClO_2. The response to final brightening with ClO_2 in the D(EPO)DED sequence was not appreciably affected by the moderate levels of stage-to-stage carryover or by inclusion of 10 kg/t of black liquor solids in the D_0 stage. Substitution of O_3 for half of the ClO_2 in the first stage had little or no effect on D_2 brightness at levels below 89.

In terms of the total ClO_2 requirement to reach 89-90 brightness, sequences may be ranked as follows: OD(EPO)DP < O(Z/D)(EPO)DP < (D/C)(EPO)DED = (D/Z)(EPO)DED = OD(EPO)DD < D(EPO)DED < OD(EPO)D. In an additional stage following an OD(EPO)D sequence, H_2O_2 and ClO_2 were equally effective on a weight basis. Ozone, however, was less effective in brightening the pulp. Low charges of peroxide were less effective after the O(D/Z)(EPO)D sequence, but substitution of O_3 for 50% of the ClO_2 in the delignification stage raised the brightness ceiling, making it possible to reach very high brightnesses with very large H_2O_2 charges.

Brightness reversion was similar for all sequences, except that sequences ending with a H_2O_2 stage gave pulps with slightly improved brightness stability and the sequence ending with an O_3 stage gave poorer brightness stability. When ranked according to pulp viscosity, the sequences fell into two homogeneous groups. The low-viscosity group included the D(EPO)DED sequences with no carryover and sequences in which O_3 was used.

Combined effluent AOX values were close to those predicted by an empirical model, which, in effect, predicts that 11-13% of the Cl atoms added in the first bleaching stage and 2% of the Cl atoms added in subsequent stages will emerge as AOX. COD values for the five-stage ECF sequences were higher than for the (D/C)-based sequence and elimination of black liquor carryover into the first stage decreased COD. The effluent from the O(Z/D)(EPO)DP sequence had the highest COD value.

All of the five-stage sequences may be expected to have virtually the same chemical cost. The bleaching of oxygen delignified pulp can probably be accomplished in three stages with no increase in cost for chemicals (excluding any cost of chemicals for the oxygen stage itself). Addition of a fourth stage employing ClO_2 may allow the oxygen delignified pulp to be bleached at a chemical cost which is roughly 20% lower than for the three-stage sequence or the five-stage nonoxygen sequence. Addition of a final H_2O_2 stage instead of a ClO_2 stage may not yield a similar saving, principally because of the associated costs for NaOH and DTPA. Using an O_3 stage at the end of the sequence does not appear feasible for the hardwood pulp used in this study, due to the high brightness reversion observed. Partial replacement of ClO_2 with O_3 increased chemical costs for the OD(EPO)DP sequence.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of this work by Air Products and Chemicals, Inc., FMC Corporation, the Georgia Traditional Industry Program in Pulp and Paper, and the Member Companies of the Institute of Paper Science and Technology.

We also thank Mark Turner of IPST for technical advice and assistance with some of the experiments, and Champion International for pulp samples and technical guidance.

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